Acid). Sodium hydroxide (5.2 g) in water (50 ml) was added with vigorous agitation over a period of 1 hr and under a nitrogen atmosphere to 2-pentyl-3-dimethylmalonylcyclopentan-1-one (**8**, 17.5 g, 0.062 mol). The reaction mixture was stirred overnight at room temperature and extracted with ether, and the aqueous layer was acidified with sulfuric acid (7 g in 15 ml of water). The aqueous layer was refluxed until gas evolution ceased. The cold solution was extracted with ether, washed with water, and dried over magnesium sulfate. The solvents were removed *in vacuo* and the residue was distilled, affording 13.3 g (95%) of 2-pentyl-3-oxocyclopentylacetic acid: bp 168–170° (0.3 mm); ir (liquid) 3070–3020, 1740, 1712, 1465, 1410, 1165 cm^{-1}; nmr (CCl_4) δ 0.85 (3 H, t), 1.05–1.65 (8 H, m), 1.84–2.74 (8 H, m), 11.2 (1 H, s).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.08; H, 9.31.

Methyl-2-pentyl-3-oxocyclopentyl Acetate (12, Methyl Dihydrojasmonate). 2-Pentyl-3-oxocyclopentylacetic acid (**9**, 2 g, 0.094 mol), dry methanol (20 ml), and *p*-toluenesulfonic acid (10.05 g) were refluxed overnight. Methanol was distilled and the residue was extracted with ether. The ether solution was washed successively with a solution of sodium chloride, sodium bicarbonate, and again with sodium chloride and dried over magnesium sulfate. Distillation yielded 1.7 g (80%) of methyl-2-pentyl-3-oxocyclopentyl acetate: bp 105–107° (0.2 mm); ir (liquid) 1740, 1440, 1269, 1170 cm^{-1}; nmr (CCl_4) δ 0.85 (3 H, t), 1.01–1.58 (8 H, m), 1.82–2.51 (8 H, m), 3.55 (3 H, s).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.72; H, 9.60.

Methyl-2-pentylcyclopent-2-en-1-ol Acetate (10). Method A. Methyl acetate (1.71 ml, 25 mmol) was added dropwise over a period of 2 min (under a nitrogen atmosphere) into a THF solution of lithium bis(trimethylsilyl)amide (25 ml, 1.0 *M*) at −78°. After the addition was completed, the stirring proceeded for 15 min. 2-Pentylcyclopent-2-en-1-one (**5**, 3.8 g, 25 mmol) was injected through a septum inlet. After a period of 15 min, hydrochloric acid (5 ml, 20%) was injected. After the reaction was completed, the mixture was extracted with hexane. The organic layer was separated, washed with a saturated solution of sodium bicarbonate and water, and dried over sodium sulfate. Hexane was distilled off and the residue was distilled under reduced pressure, yielding 4.63 g (82%) of methyl-2-pentylcyclopent-2-en-1-ol-acetate: bp 97° (0.4 mm); ir (liquid) 3500, 1740, 1440, 1203 cm^{-1}; nmr (CCl_4) δ 0.93 (3 H, t), 1.13–1.50 (8 H, m), 1.71–2.24 (4 H, m), 2.42 (2 H, s), 2.52 (2 H, s), 3.31 (1 H, s), 3.69 (3 H, s), 5.42 (1 H, m).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 69.03; H, 9.74. Found: C, 69.10; H, 9.47.

Method B. 2-Pentylcyclopent-2-en-1-one (**5**, 1.52 g, 10 mmol) and methyl bromoacetate (1.1 ml, 10 mmol) in dry benzene (8 ml) were added slowly to activated zinc (0.65 g, 0.02 g-atom) in boiling benzene (2 ml). After the exothermic reaction had subsided, the mixture was refluxed for 30 min and cooled and acetic acid (5 ml, 10%) was added. The benzene layer was separated, washed with a solution of sodium bicarbonate and water, and dried over sodium sulfate. The solvent was removed *in vacuo* and the residue was distilled under reduced pressure affording 1.36 g (60%) of the product, bp 97° (0.4 mm), ir and nmr identical with those obtained by method A.

Methyl-2-pentyl-3-oxo-1-cyclopentenyl Acetate (11). Chromium trioxide (1 g) in sulfuric acid (10 ml, 5%) was added dropwise at 0° to methyl-2-pentylcyclopent-2-en-1-ol acetate (**10**, 2.03 g, 9 mmol) in ether (30 ml). After the addition was completed, the stirring proceeded for 45 min at 5°. Water was added and the product was extracted with hexane. The organic layer was separated, washed with a solution of sodium bicarbonate (10%) and water, and dried over sodium sulfate. The solvent was evaporated and the oil was distilled, affording 1.75 g (87%) of methyl-2-pentyl-3-oxo-1-cyclopentenyl acetate: bp 118–119° (0.4 mm); ir (liquid) 1740, 1705, 1645, 1435, 1175 cm^{-1}; uv (EtOH) 237 nm (ϵ 9200); nmr (CCl_4) δ 0.88 (3 H, t), 1.15–1.41 (8 H, m), 2.01–2.80 (4 H, m), 3.35 (2 H, s), 3.68 (3 H, s).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.64; H, 8.93. Found: C, 69.73; H, 9.20.

Methyl-2-pentyl-3-oxocyclopentyl Acetate (12, Methyl Dihydrojasmonate). Methyl-2-pentyl-3-oxo-1-cyclopentenyl acetate (**11**, 115 mg, 0.51 mmol), with sodium hydroxide (0.05 g) and methanol (15 ml) in the presence of Pd/C (0.21 g, 5%), was hydrogenated at room temperature. After the hydrogenation was completed, the catalyst was removed by filtration and the methanol was evaporated *in vacuo*. Methyl dihydrojasmonate (50 mg, 43%) was obtained by preparative glc. Its spectroscopic (ir, nmr) and chromatographic (glc) data were identical with those of methyl dihydrojasmonate prepared from compound **9**.

Registry No.—**1**, 611-10-9; **2**, 24852-03-7; **3**, 4819-67-4; **4**, 24851-93-2; **5**, 25564-22-1; **6**, 1128-08-1; **7**, 13074-63-0; **8**, 51806-23-6; **9**, 3572-64-3; **10**, 51806-24-7; **11**, 24863-70-5; **12**, 24851-98-7.

References and Notes

(1) T. Yoshida, A. Yamaguchi, and A. Komatsu, *Agr. Biol. Chem.*, **30**, 370 (1966).
(2) G. Stork, F. Rouessac, and O. Gringore, *J. Amer. Chem. Soc.*, **93**, 3091 (1971).
(3) J. E. McMurry and J. Melton, *J. Amer. Chem. Soc.*, **93**, 5309 (1971).
(4) P. A. Grieco, *J. Org. Chem.*, **37**, 2363 (1972).
(5) H. C. Ho, T. L. Ho, and C. M. Wong, *Can. J. Chem.*, **50**, 2718 (1972).
(6) E. Demole and M. Stoll, *Helv. Chim. Acta*, **45**, 692 (1962).
(7) K. Sisido, S. Kurozumi, and K. Utimoto, *J. Org. Chem.*, **34**, 2661 (1969).
(8) G. Büchi and B. Egger, *J. Org. Chem.*, **36**, 2021 (1971).
(9) J. L. E. Erickson and F. E. Collins, *J. Org. Chem.*, **30**, 1050 (1965).
(10) R. T. Dahill, *J. Org. Chem.*, **31**, 2694 (1966).
(11) J. Ficini, J. D'Angelo, and J. P. Genêt, *Tetrahedron Lett.*, 1569 (1971).
(12) S. M. Supta and S. S. Deshapanda, *J. Indian Chem. Soc.*, **30**, 23 (1963).
(13) J. Bagli and T. Bogri, *Tetrahedron Lett.*, 3815 (1972).
(14) J. Bagli, T. Bogri, R. Deghenghi, and K. Wiesner, *Tetrahedron Lett.*, **No. 5**, 465 (1966).
(15) P. L. Stotter and K. A. Hill, *J. Org. Chem.*, **38**, 2576 (1973).
(16) K. Oshima, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, **95**, 4446 (1973).
(17) E. Demole, E. Lederer, and D. Mercier, *Helv. Chim. Acta*, **45**, 685 (1962).
(18) M. W. Rathke, *J. Amer. Chem. Soc.*, **92**, 3222 (1970).

Synthesis of Some Bridged Triterpene Ethers[1a]

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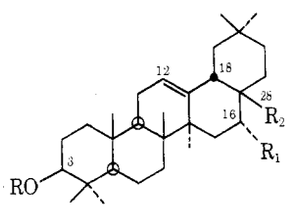
Received January 29, 1974

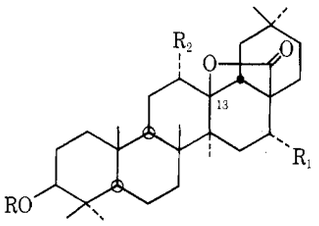
Several 13β,28-epoxyoleananes with additional oxygen functions in the molecule have recently been isolated from plants.[2-10] An unambiguous synthesis of the simplest of these, protoprimulagenin A (**21**), was desired to confirm this structural feature.

Although protoprimulagenin A was isolated from *Primula sieboldi* roots as recently as 1968,[10] Tschesche and coworkers had prepared such a compound from echinocystic acid (**3**) in 1964.[3,5] By heating in acetic and concentrated hydrochloric acids for several hours, **3** was converted to a 13β,28-lactone which was then reduced to a 13β,28-epoxide with boron trifluoride etherate and lithium aluminum hydride.[3]

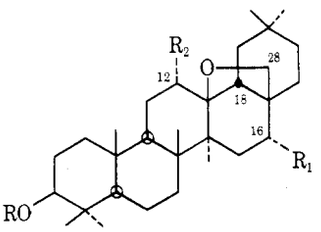


1, R = R_1 = H; R_2 = CO_2H
2, R = R_1 = H; R_2 = CO_2CH_3
3, R = H; R_1 = OH; R_2 = CO_2H
4, R = H; R_1 = OH; R_2 = CO_2CH_3
5, R = Ac; R_1 = OAc; R_2 = CO_2H
6, R = R_1 = H; R_2 = CH_2OH
7, R = Ac; R_1 = H; R_2 = CH_2OH
8, R = R_1 = H; R_2 = CH_2OAc
9, R = Ac; R_1 = H; R_2 = CH_2OAc
10, R = H; R_1 = OH; R_2 = CH_2OH
11, R = H; R_1 = OH; R_2 = CH_2OH
with Br at 12 or OH at 13

However, it is reported that heating an olean-12-en-28-oic acid with acetic and concentrated hydrochloric acids is liable to produce **13** rather than **12**.[11] There is no appreciable difference between the specific rotations of the two and unless both are known and have different melting points it is not easy to distinguish between them. We therefore prepared the epoxide through a route which is certain to retain the 18β-H stereochemistry of **3**.



12, R = R_1 = R_2 = H
13, R = R_1 = R_2 = H($C_{18}\alpha$-H)
14, R = Ac; R_1 = OAc; R_2 = Br
15, R = R_2 = H; R_1 = OH
16, R = H; R_1 = OH; R_2 = Br
17, R = Ac; R_1 = OAc; R_2 = H



18, R = R_1 = R_2 = H
19, R = Ac; R_1 = R_2 = H
20, R = R_1 = H; R_2 = Br
21, R = R_2 = H; R_1 = OH

Olean-12-en-28-oic acids are known to give oleanane-12α-bromo-13β,28-lactones on treatment with bromine in acetic acid.[12] As these bromolactones are readily converted to the parent acid on treatment with zinc and acetic acid,[12] this mode of preparation of an oleanane bromolactone ensures the retention of stereochemistry at position 18. Before starting the synthesis we made sure that no isomerization would take place in any of the subsequent steps as well by effecting the following transformations.

Oleanolic acid **1** was first converted to the known lactone **12** by passing dry HCl gas through a chloroform solution. This procedure has been shown to retain the 18β-H stereochemistry of **1**.[11] Reduction of **12** with lithium aluminum hydride and boron trifluoride etherate[13] gave the epoxy compound **18** as characterized by its spectral properties and elemental analysis. Acetylation of **18** gave the 3-monoacetate **19**. Treatment of **19** with boron trifluoride etherate in benzene gave a quantitative yield of a monoacetate monoalcohol, which from its mode of formation and spectral properties was assigned the structure **7** of erythrodiol-3-monoacetate.[14] This was confirmed by acetylating **7** to the diacetate **9** identical with that obtained by acetylating erythrodiol **6**.[15] As **6** is obtained by reducing **2** with $LiAlH_4$, **6** has its 18-H β oriented. Thus these reaction sequences prove that in the reaction with HCl gas in chloroform at room temperature, or with boron trifluoride etherate and lithium aluminum hydride, or with boron trifluoride etherate in benzene, no epimerization at position 18 takes place.

The conversion of **19** to **7** as indicated above is an unambiguous method of preparing the pure 3-monoacetate **7**.

In an attempt to prepare **18** directly from **6**, the latter was treated with dry HCl gas in acetic acid at room temperature for 15 min. The product isolated, however, was a monoacetate of **6** different from **7**, which therefore must be the 28-acetate **8**. This was confirmed by further acetylating **8** to give **9** identical in all respects with the authentic sample. This procedure could be useful in selectively acetylating a primary alcohol in the presence of secondary alcohols.

Treatment of **6** with bromine in acetic acid gave a product in about 50% yield which was characterized as **20** by its spectral and other properties. Reduction of **20** with lithium aluminum hydride gave **18** identical with that obtained before. As **18** has already been shown to retain the stereochemistry of the 18-H, that is, β, this sequence of reactions gives independent proof that the cyclization from C_{28} to C_{13} by bromination does not isomerize the 18β-H.

Reduction of **4** with lithium aluminum hydride gave **10**.[16,17] An attempt to convert **10** directly to **21** by passing dry HCl gas through a chloroform solution was not successful.

Similarly attempted bromination of **10** with bromine in acetic acid yielded only the starting material. Although the bromolactone **16** was prepared from **3** with bromine in acetic acid, it was barely soluble in the solvents used for the $LiAlH_4$ reduction, and consequently its reduction did not yield the desired product **21**.

Hence **5** was converted to **14**[18] and reduced with boron trifluoride etherate and lithium aluminum hydride to give **21**, which, as discussed previously, should definitely have its 18-H β oriented. This compound was found to be identical with protoprimulagenin A (**21**) by its spectral properties, R_f value in tlc, and melting point and mixture melting point with an authentic sample.[10]

Experimental Section[19]

3β-Hydroxy-13β,28-epoxyoleanane (18). The lactone **12** was prepared by passing HCl gas for 15 min through a $CHCl_3$ solution of **1**.[11] To a stirred suspension of $LiAlH_4$ (150 mg) in dry ether (20 ml) kept at 0° was added during the course of 15 min a solution of **12** (300 mg) in dry ether (30 ml) containing boron trifluoride etherate (3 ml). Stirring was continued for 2 hr at 0–5° and for 8 hr at room temperature. The reaction was then quenched at 0° with a saturated $NaHCO_3$ solution and the excess $LiAlH_4$ was destroyed with ethyl acetate, ice, and sodium potassium tartrate. Extraction with ether (295 mg) and chromatography over basic alumina (20 g) gave in ethyl acetate–benzene (8:92) **18** (98 mg): mp 229°; $[\alpha]D$ +2°; M^+ *m/e* 442; ir, transparent in the carbonyl region; nmr δ 3.15, 3.45 (AB q, J = 8 Hz, 2 H) and absence of vinyl proton. *Anal.* Calcd for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found: C, 81.27; H, 11.48. Further elution with ethyl acetate–benzene (15:85) gave erythrodiol **6** (60 mg), mp 234°, $[\alpha]D$ +76°, and oleanolic acid **1** (20 mg), mp 310°, $[\alpha]D$ + 77°. Compounds **6** and **1** were identified by direct comparison (tlc, ir, nmr, mixture melting point) with authentic samples.

The acetate **19** prepared from **18** showed mp 222°; $[\alpha]D$ +0.3°, M^+ *m/e* 484; ν_{max} 1725 and 1250 cm^{-1}; nmr δ 2.2 (s, 3 H), 3.18 and 3.48 (AB q, J = 8 Hz, 2 H), 4.5 (m, 1 H), and absence of vinyl proton. *Anal.* Calcd for $C_{32}H_{52}O_3$: C, 79.28; H, 10.81. Found: C, 79.21; H, 10.83.

28-Hydroxyolean-12-en-3β-yl Acetate (7). To a solution of **19** (50 mg) in dry benzene (2 ml), boron trifluoride etherate (0.01 ml) was added. After 10 min the reaction was quenched with $NaHCO_3$ solution. Extraction with ether and crystallization from ether–methanol furnished **7** (45 mg):[14] mp 238°; $[\alpha]D$ +73° (lit.[14] mp 238.5–239°; $[\alpha]D$ +71°); M^+ *m/e* 484; ν_{max} 1725, 1240, and 3505 cm^{-1}; nmr δ 5.1 (s, br, 1 H), 4.5 (m, 1 H), and 3.35 (q, 2 H). Acetylation in the usual way gave the diacetate: mp 186°; $[\alpha]D$ +64° (lit.[14] mp 186°; $[\alpha]D$ +66.7°); M^+ *m/e* 526; ν_{max} 1720 and 1240 cm^{-1}; nmr δ 5.1 (s, br, 1 H), 2.1 (s, 6 H). It was identical with an authentic sample of **9** prepared by reducing **2** with $LiAlH_4$ and subsequent acetylation.

3β-Hydroxyolean-12-en-28-yl Acetate (8). HCl gas was bubbled through a solution of **6** (1 g) in acetic acid (25 ml) for 15 min at room temperature and the solution was poured into water. Extraction with ether and chromatography over basic alumina (40 g) gave **8** (104 mg): mp 196°; $[\alpha]D$ +36.8°; M^+ *m/e* 484; ν_{max} 1748,

1230, and 3500 cm^{-1}; nmr δ 2.1 (s, 3 H) and 5.1 (s, br, 1 H). *Anal.* Calcd for $C_{32}H_{52}O_3$: C, 79.28; H, 10.81. Found: C, 79.45; H, 10.75. This was converted to the diacetate **9** (pyridine, acetic anhydride), mp 186°, $[\alpha]D$ +64°, M^+ *m/e* 526, identified by direct comparison (tlc, ir, nmr, mixture melting point) with an authentic sample.

3β-Hydroxy-13β,28-epoxy-12α-bromooleanane (20). A solution of bromine in acetic acid (3%, 4.5 ml) was added dropwise to a stirred solution of **6** (500 mg) and NaOAc (2.0 g) in 90% aqueous acetic acid (50 ml). After 3 hr the solution was poured into water containing $Na_2S_2O_3$. Usual work-up furnished **20** (250 mg): mp 180°; $[\alpha]D$ +3.6°; M^+ *m/e* 520; ν_{max} 3400 cm^{-1}; nmr δ 4.3 (m, 1 H), 3.5 (q, 2 H), and no vinyl proton signal. *Anal.* Calcd for $C_{30}H_{49}BrO_2$: C, 69.1; H, 9.5. Found: C, 68.9; H, 9.6.

3β-Hydroxy-13β,28-epoxyoleanane (18) from 20. A solution of **20** (50 mg) in THF (5 ml) was added to a refluxing slurry of $LiAlH_4$ (50 mg) in THF (25 ml). Refluxing and stirring were continued for 8 hr. Usual work-up and crystallization from ether–methanol yielded **18** (15 mg), mp 229°, $[\alpha]D$ +1.9°, M^+ *m/e* 442, identified by tlc, nmr, melting point, and mixture melting point with an authentic sample.

Echinocystic Acid[20] Bromolactone (16). A solution of bromine in acetic acid (3%, 2–3 ml) was added dropwise during the course of 3 hr to a stirred solution of **3** (100 mg) and NaOAc (400 mg) in 90% aqueous acetic acid (10 ml). The reaction mixture was then poured into water containing $Na_2S_2O_3$. The crystalline material was filtered (45 mg) and recrystallized from $CHCl_3$–MeOH to yield **16** (30 mg): mp 246°; $[\alpha]D$ +61°; M^+ *m/e* 550; ν_{max} 1750 cm^{-1}; nmr δ 4.3 (m, 1 H) and absence of vinyl proton signal. *Anal.* Calcd for $C_{30}H_{47}BrO_4$: C, 65.31; H, 8.59. Found: C, 65.62; H, 8.81.

Reduction of 16 (200 mg) with boron trifluoride etherate (2 ml) and $LiAlH_4$ (200 mg) in THF (25 ml) for 8 hr yielded a mixture (185 mg) whose ir spectrum was transparent in the carbonyl region. Its nmr spectrum showed signals at δ 4.3 (m, 1 H) and 3.3 (2 H) and no vinyl proton signal. This was again reduced with $LiAlH_4$ (150 mg) in refluxing THF (30 ml) for 7 hr to yield a mixture (170 mg) which on chromatography on alumina (10 g) did not yield **21** but furnished **10** (38 mg), mp 242°, $[\alpha]D$ +41°, identified by direct comparison (tlc, ir, mixture melting point) with an authentic sample prepared by reducing **4** with $LiAlH_4$. It also gave a compound (34 mg), mp 168–170°, which was not **11** and was not further characterized.

A solution of **10** (200 mg) in $CHCl_3$ (15 ml) was treated with gaseous HCl for 1 hr at room temperature. Usual work-up gave a solid (185 mg) which on chromatography on alumina (10 g) furnished the starting material (98 mg) and another product (48 mg), mp 246°, M^+ *m/e* 486, which was not further characterized.

Echinocystic Acid Lactone (15). A stream of gaseous HCl was passed through a solution of **3** (100 mg) in $CHCl_3$ (50 ml) for 15 min at room temperature. Removal of the unreacted acid with 15% aqueous KOH yielded the neutral **15** (23 mg): mp 280°: $[\alpha]D$ +14°; ν_{max} 1753 cm^{-1}; nmr spectrum showed the absence of vinyl protons. *Anal.* Calcd for $C_{30}H_{48}O_4$: C, 76.22; H, 10.24. Found: C, 76.31; H, 10.41. Reduction of **15** with boron trifluoride etherate and $LiAlH_4$ did not give **21**.

Protoprimulagenin A (21). A solution of **14**[18] (300 mg) in THF (20 ml) containing boron trifluoride etherate (3 ml) was added to a stirred suspension of $LiAlH_4$ (250 mg) in THF (250 ml) at 0°. Stirring was continued for 2 hr at ice-bath temperature. Usual work-up and chromatography on basic alumina gave in benzene–ethyl acetate (1:1) **21** (48 mg): mp 262°; $[\alpha]D$ +22°; ν_{max} 3600–3500 cm^{-1}; nmr δ 3.1–3.5 (m, 3 H) and 3.91 (1 H). This was identified by direct comparison (tlc, ir, nmr, mixture melting point, etc.) with an authentic sample.[10]

Acknowledgments. We are indebted to Professor I. Kitagawa for an authentic sample of protoprimulagenin A and to the CSIR (India) for the award of a junior research fellowship to one of us (A. A. N.).

Registry No.—**3**, 545-88-0; **6**, 545-48-2; **7**, 7089-38-5; **8**, 51820-71-4; **12**, 1721-60-4; **14**, 51830-03-6; **15**, 51829-67-5; **16**, 51829-68-6; **18**, 35738-40-0; **19**, 43059-47-8; **20**, 39701-58-1; **21**, 2611-08-7.

References and Notes

(1) (a) National Chemical Laboratory Communication No. 1818. (b) Institut de Chimie, Université Louis Pasteur, Strasbourg, France.
(2) K. Venkateswara Rao, *Tetrahedron*, **20**, 973 (1964).
(3) R. Tschesche, F. Inchaurrondo, and G. Wulff, *Justus Liebigs Ann. Chem.*, **680**, 107 (1964).
(4) R. Tschesche, H. Striegler, and H. W. Fehlhaber, *Justus Liebigs Ann. Chem.*, **691**, 165 (1966).
(5) R. Tschesche, B. Tjiong Tjoa, and G. Wulff, *Justus Liebigs Ann. Chem.*, **696**, 160 (1966).
(6) N. Aimi and S. Shibata, *Tetrahedron Lett.*, 4721 (1966).
(7) I. Yosioka, T. Nishimura, N. Watani, and I. Kitagawa, *Tetrahedron Lett.*, 5343 (1967).
(8) T. Kubota and H. Hinoh, *Tetrahedron Lett.*, 4725 (1966); *Tetrahedron*, **24**, 675 (1968).
(9) R. O'Dorchai and J. B. Thomson, *Tetrahedron Lett.*, 2223 (1965); *Tetrahedron*, **24**, 1377 (1968).
(10) I. Kitagawa, A. Matsuda, and I. Yosioka, *Tetrahedron Lett.*, 5377 (1968).
(11) D. H. R. Barton and N. J. Holness, *J. Chem. Soc.*, 78 (1952).
(12) See, *e.g.*, F. E. King, T. J. King, and J. M. Ross, *J. Chem. Soc.*, 3995 (1954); 1333 (1955).
(13) G. R. Pettit and T. R. Kasturi, *J. Org. Chem.*, **26**, 4557 (1961).
(14) V. Prelog, J. Norymberski, and O. Jeger, *Helv. Chim. Acta*, **29**, 360 (1946).
(15) C. Djerassi, R. M. McDonald, and A. J. Lemin, *J. Amer. Chem. Soc.*, **75**, 5940 (1953).
(16) B. Bischof, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **32**, 1911 (1949).
(17) D. H. R. Barton, A. Hameed, and J. F. McGhie, *J. Chem. Soc.*, 5176, 5182 (1962).
(18) W. R. White and C. R. Noller, *J. Amer. Chem. Soc.*, **61**, 984 (1939); C. Sannie, H. Lapin, and I. P. Varshney, *Bull. Soc. Chim. Fr.*, 1440 (1957).
(19) Melting points are uncorrected and were taken in capillary tubes in a Gallenkemp melting point apparatus. Optical rotations were determined in 1% $CHCl_3$ solution on a Perkin-Elmer spectropolarimeter. Ir spectra were recorded on a Perkin-Elmer Model 221 or Infracord spectrophotometer in $CHCl_3$ solution. Nmr spectra were determined on a Varian A-60 or T-60 spectrometer in $CDCl_3$ solution using TMS as an internal standard. Mass spectra were recorded on a CEC Model 21-110 B mass spectrometer at 70 eV, by direct inlet system. Tetrahydrofuran (THF) was distilled over lithium aluminum hydride.
(20) Echinocystic acid (**3**) was isolated from the seeds of *Albizzia lebbek* by the procedure of I. P. Varshney, *Indian J. Chem.*, **7**, 446 (1949).

Nucleophilic Addition of Aliphatic Hydroxylamines to *p*-Tolylsulfonylacetylenes. Competitive Nitrogen and Oxygen Attack

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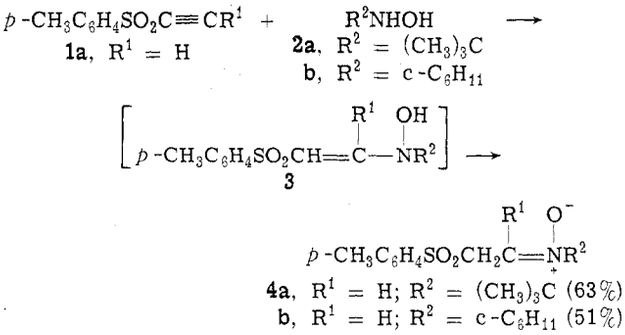
Received March 14, 1974

Acetylenes activated by sulfonyl substitution at the triple bond usually undergo facile nucleophilic addition.[1-4] Particularly the addition reactions of primary and secondary amines have been subjected to detailed investigation. However, there seems to be no literature precedent for the reaction of hydroxylamines with acetylenic sulfones. We report here a few examples of such reactions.

When *p*-tolylsulfonylacetylene (**1a**) was allowed to react with *N*-*tert*-butylhydroxylamine (**2a**) or *N*-cyclohexylhydroxylamine (**2b**) in ethanol at room temperature, a smooth reaction occurred. The analytical and spectral properties of the crystalline products obtained were entirely consistent with the nitrone structures[5] **4a,b**. The pres-



ence of a nitrone functionality in **4a,b** is further supported by the successful utilization of these compounds as spin